
(12) UK Patent Application (19) GB (11) 2 115 013 A

(21) Application No 8301268
(22) Date of filing 18 Jan 1983
(30) Priority data
(31) 341966
(32) 22 Jan 1982
(33) United States of America (US)

(43) Application published
1 Sep 1983

(51) INT CL³

C09K 13/06

(52) Domestic classification
C7E 118 120 126 130
172 208 216 218 224
C7D 15
U1S 1471 1480 1592
1989 C7D C7E

(56) Documents cited

GB 1607726

GB 1448366

GB 1420578

GB 1283483

GB 1166866

GB 1109743

GB 0892064

(58) Field of search

B6J

C7B

C7D

C7E

C7U

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(54) Composition for selective chemical removal of hard surface coatings from superalloy substrates

(57) The composition comprises an aqueous solution of H₂SO₄, a nitro-substituted aromatic compound, and optionally a fluoride ion producing species, and a surfactant. The

composition can selectively remove hard surface layers deposited through flame, plasma spray, and detonation gun techniques on superalloy substrates by contacting the above stripping solution in a heated bath wherein the bath is continuously agitated by an ultrasonic agitation means.

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SPECIFICATION

Selective chemical removal of hard surface coatings from superalloy substrates

This invention is related to the removal of ceramic, cermet and metallic coatings from high strength, high temperature resistant metal substrates and, more particularly, to the removal of these hard surface coatings from superalloys, particularly nickel-base substrates by use of an aqueous acidic stripper bath equipped with a high energy density agitation means.

One of the most difficult requirements in the chemical stripping art has been to develop a composition which will chemically remove the "hard surface" coatings, that is, molten particle coatings which are applied by detonation gun, plasma, and flame spray methods onto metal surfaces, such as the nickel-base jet engine combustion chambers. Such coatings, which are usually applied in thin layers to provide protection against high temperature oxidative gas streams, include heat resistant ceramics, cermets, and nickel-base mixtures.

The Prior Art has lacked an efficient chemical stripper which can quickly and selectively remove such coatings without damaging the underlying substrate. Currently used techniques feature mechanical methods such as machining, grinding and abrasive blasting the coating, and non-mechanical methods such as chemical immersion in solutions which only soften a ceramic coating, e.g. hydrochloric acid base solutions, and the use of molten salt baths. However, mechanical methods are very time consuming, and additionally can easily damage a very expensive piece of equipment, due to the ease in creating extensive dimensional damage on the metal substrate, which is frequently used in a "high technology" application. Although current chemical methods will soften certain ceramic coatings, subsequent mechanical removal of the ceramic, along with the underlying inner bond coating is still required. Molten salt baths are hazardous to operate, and are effective on only a limited number of coating substrate combinations. Also these techniques are all deficient in their speed of removal, cost of operation, and effectiveness of result. U.S. Patent 2,698,781 discloses sulfuric acid solutions containing nitroaromatic additives which are effective in removing oxide scale and electroplated nickel from copper substrates. However, there is no teaching inferring that ceramic, cermet or hard surface metallic coatings might be chemically removable from a nickel-base substrate.

It is an object of this invention to create an effective composition and accompanying method for the removal of hard surface coatings from high strength, high temperature resistant alloy substrates.

It is another object of this invention to create an effective composition and accompanying method for the selective, non-corrosive removal of hard, high temperature resistant ceramics, cermets and nickel-base bond coats from nickel-base substrates.

It is still another object of this invention to devise a method of selectively stripping only the hard surface coating from jet engine component metal surfaces without dimensional damage to the stripped metal surfaces.

These and other objects of the invention have been accomplished by the discovery of a novel composition and accompanying method for the selective removal of hard surface coatings particularly heat resistant ceramic, cermets and nickel-base coats, from high strength, high temperature resistant metal substrates, in particular nickel-base substrates. The stripping composition comprises H_2SO_4 , preferably about 90—450 grams/liter (g/l) of concentrated H_2SO_4 , e.g., 66° Be' @ 1.84 spec. grav., most preferably about 250—300 g/l; about 20 g/l to saturation of a water soluble, nitro-substituted aromatic compound, and most preferably about 100—120 g/l of meta-nitrobenzene sodium sulfonate; about 0—70 g/l of a water soluble, fluorine-containing species, most preferably about 10—20 g/l of fluoroboric acid; about 0—1.0 g/l of a surfactant, most preferably about 0—.5 g/l of one of the group of diphenylether sulfonates; the remainder being water in amount of about 2—90 wt. % of the solution. The stripping method of the invention involves contacting the hard surface coatings, usually a heat resistant ceramic, cermet, or nickel-base coating on the metal substrate with the acidic stripping solution described above, preferably comprising sulfuric acid, a soluble fluorine-containing species, a soluble nitro-substituted aromatic compound, a surfactant and water, and continuing the contacting until the hard surface coating has been selectively removed from the metal surface. The contacting is carried out by immersing the deposited substrate in the solution bath which is kept at about 120—180°F., most preferably about 130—150°F., as the bath is actively agitated by an ultrasonic agitation means, most preferably an adequately powered ultrasonic generator-transducer, to a power density of at least about 4 watts/in², and preferably about 7—8 watts/in². Upon complete coating removal, the substrate is removed from the solution, rinsed, and is in condition for further processing.

A well known technique, particularly in the "high technology" industries involving the construction of jet engines, and gas turbine engines which employ superalloys that are useful, for example, in aeronautical applications, is to coat the metal surfaces which will be exposed to severe high temperature oxidation environments with a thin, i.e., a few mils, coatings of a protective metallic or nonmetallic layer. These coatings, commonly referred to as "hard surface" coatings, can be any one of a number of high strength heat and corrosion resistant substances, and usually include a "nickel-base", hereinafter defined as "a metallic mixture rich in nickel which can function as both a bonding coat for a protective ceramic layer, or, the protective layer itself"; a ceramic substance, or a cermet, as well as certain mixtures of these substances. One particularly hard coating which is frequently used on

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aircraft combustion chambers as a protective coating is a three layer system, which has the following composition:

5	Bond Coat:	3—5 mils, Ni 80%, Cr 15%	5
	Intermediate Coat:	4—6 mils, 35—65% mixture of Ni 80%—Cr 20% and MgO—ZrO ₂	
	Outer Coat:	6—10 mils MgO—ZrO ₂ .	

Other hard surface coatings which are finding application in jet engine combustion chambers and are of particular note are:

10	A: Co 23, Cr 18, Al 12, Y 5, Ni balance;	10
	B: Y stabilized zirconia;	
	C: Co Cr Al Y;	
	D: Ni+Cr 94, Al 6, Yl.	

These hard surface coatings which can be stripped from a variety of metal substrates which, in the broadest embodiment of the invention, can be of any metal which is resistant to acid or alkaline corrosion, and more specifically, metal superalloys which have both high temperature resistance and high strength at these elevated temperatures. In particular, alloys located in the VIII A Group on the Periodic Chart, i.e., iron, nickel and cobalt, and particularly nickel-base alloys, such as the well known "Hastelloy X" are stripped of their coatings by the composition of the invention. The coatings are applied to the substrates through a variety of well known techniques in the art, e.g., detonation gun, plasma spray, and flame spray particle applications, which all essentially consist of grinding the compositions into a fine powder, heating the powder up into its molten form, and spraying the molten material, which has been accelerated in a gas plasma to high speeds, onto the substrate to be coated in the form of a fine, very thin metal mist, which hardens to form an extremely tough, protective coating.

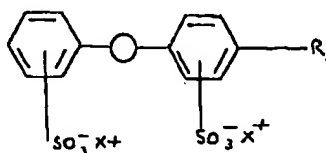
This invention is further directed to an improved composition and accompanying method of removal of these coatings which have been applied in the above-described manner. In order for a strong chemical stripper to function effectively several problems must first be overcome. The stripping composition must be able to strip at a satisfactory rate, e.g., of the order of 1/2—2 mils per hour, and must be carefully ventilated so as to remove toxic vapors resulting from the process, which is always a major consideration when dealing with chemicals in this art, both in the lab and in their industrial environments and applications. Such a solution has been found by creating an aqueous acidic bath having the following composition: Sulfuric acid, H₂SO₄, preferably in its concentrated form, e.g., 66 Be', although any commercially available brand is satisfactory, is an essential constituent of the solution. The concentration of H₂SO₄ should range between about 90—450 g/l, and preferably between about 250—300 g/l. Too little acid will not give the bath the necessary acid strength to remove the coatings at a suitable rate, while amounts in excess of 450 g/l do not provide additional superior stripping results and cannot be economically justified; however, in theory, H₂SO₄ could consist of as much as 90% of the solution.

A second, essential element in the stripping solution, functioning as an oxidizing agent, is, in the broadest embodiment of the invention, a water soluble nitro-substituted aromatic compound, or, more preferably, a water soluble nitro-substituted benzene compound such as the class of compounds disclosed in U.S. Patent 2,698,781. Most preferably, meta-nitrobenzene sodium sulfonate or sulfonic acid, or the like, e.g., any suitable alkali or alkaline earth metal nitrobenzene sulfonate, including the ammonium radical as a functional equivalent thereof, will function effectively. This class of chemicals is believed to function in solution as a kinetic accelerator, although applicants' do not wish to be bound by theory.

The concentration of the nitro-substituted aromatic constituent can range from about 20 g/l to saturation, and should range between about 20—120 g/l, with the higher levels, e.g., 60—120 g/l, being the most preferred.

Another constituent of the bath which although not essential is highly preferred, is the addition of a soluble fluorine-containing species, most preferably fluoroboric acid, HBF₄, but other fluorine-containing species, e.g., HF, NH₄HF₂, Na₃AlF₆, et al, that can disassociate in aqueous solution to generate low fluoride ion concentrations, are particularly suitable. The concentration of the fluorine-containing species is determined by how much of it is required to produce a desired concentration of fluoride ions in solution; and generally will range between about 0—70 g/l, and preferably, about 10—20 g/l for substances which highly disassociate in aqueous solution. As the concentration of fluoride ions increase, the chance of harmful corrosion to the substrate rises, creating an upper limit barrier on the amount which can be added to the stripping solution.

It is preferred, although not essential, to include a small amount, e.g., 0—3.0 g/l and most preferably about 0—1.0 g/l of a surfactant to function as a wetting agent on the surface to be dissolved. Compounds which are particularly preferred for this task are the diphenylether sulfonates, e.g., compounds having the generic formula



where R is an alkyl group or hydrogen, and X is an alkali metal, such as sodium. Such a product is currently sold under the trade name "Dowfax 3B2", marketed by the Dow Chemical Co., Midland, Michigan. Most alkali metal diphenylether sulfonates are suitable equivalents, and, in the broadest embodiment of the invention, any surfactant which possesses hydrolytic and oxidative stability toward the stripping solution is an acceptable substitute. The stripping composition is completed by adding water, in amounts ranging from 2—90 wt. %, to bring the solution to the desired strength. Water lowers the viscosity of the stripping solution and increases the mobility of ionic species in solution.

The addition of water to sulfuric acid has the desirable effect of lowering the solution cavitation threshold, i.e., the minimum power required to reduce the local pressure on a liquid to a value less than its vapor pressure. This arises through an increase in vapor pressure and decrease in viscosity and density upon dilution. For room temperature water at 20 KHz, the cavitation threshold is 2.45 W/in².

The method of this invention involves contacting the hard surface coating with the acidic stripping solution, and continuing the contacting until the hard coating has been substantially removed from the metal substrate without any dimensional change occurring to the underlying surface. In order for the stripping to occur at an acceptable rate, it is essential that the solution bath be continually agitated by a suitable agitation means, and preferably by an ultrasonic generator-transducer, either a magnetostrictive (preferred) or a piezoelectric transducer. The transducer should operate in such a manner so as to produce a minimal power density of about 4 watts/in², and preferably about 7—8 watts/in². Stirring by conventional techniques simply will not produce the required solution agitation in the stripper bath needed to produce an effective rate. Coupled with the ultrasonic agitator, which inherently will supply energy to the solution, it is necessary to keep the solution at a temperature range of about 110—180°F in order to produce an acceptable rate of stripping, and most preferably about 130—150°F during operation.

The invention is now illustrated by the following examples which are not intended to be limiting.

Example I

An aircraft combustor used in jet engines is made of Hastelloy-X (22 Cr, 18.5 Fe, 9.0 Mo, 1.5 Co, 0.6 W, balance Ni) and plasma flame sprayed with a triple layer coating over 520 in², comprised of a bond coat, 3—5 mils thickness, Ni/Cr 95% intermediate coat, 4—6 mils, 35—36% mixture of Ni 80%—Cr 20% and MgO—ZrO₂; outer coat, 6—10 mils, MgO—ZrO₂. Two of these combustion chambers were stripped of their coatings in 10 and 16 hours, using ultrasonic agitation in a bath kept at a temperature range of 120—170°F. A 30 gallon stainless steel hot water tank containing two 1200 watt side mounted immersible ultrasonic transducers was employed during the stripping operation and 6 gallons of the stripping solution (275 g/l H₂SO₄ 66° Be', 14 g/l HBF₄ (48%), 120 g/l m-nitrobenzene sodium sulfonate, 0.1 g/l Dowfax 3B2) contained in a square polypropylene container was used. Metallagraphic examination failed to show any suitable degradation of the combustion can chambers.

Example II

A military jet engine combustion can chamber was immersed in a stripping solution containing 275 grams/liter concentrated sulfuric acid H₂SO₄ (66° Be'), 145 grams/liter fluoroboric acid, HBF₄ (48%), and 116 grams/liter meta-nitrobenzene sodium sulfonate. After 20 hours at 130—170°F, the three layer coating had been removed from the burner can. A 5 gallon stainless steel tank, fitted with a 1000 watt bottom-mounted ultrasonic transducer, containing 2 gallons of the stripping solution, in a square polypropylene container was used. No substrate degradation was observed.

Example III

A Hastelloy-X coupon with Metco 443 (Ni/Cr 93, 6 Al), a product of Metco Inc., Westbury, N.Y., was immersed into a stripping solution containing 90 grams/liter concentrated sulfuric acid H₂SO₄ (66° Be'), 72 grams/liter meta-nitrobenzene sodium sulfonate, 46 grams/liter sodium sulfate Na₂SO₄, and 1.2 grams/liter ammonium thiocyanate NH₄SCN. After 45 minutes with ultrasonic agitation at 145—150°F the several mil thick coating had been removed from the coupon.

This invention is capable of removing not only ceramics, cermets and nickel-base substances from metals, particularly nickel base superalloy substrates, without causing unacceptable dimensional changes or structural changes to the base metal, but also of removing a wide variety of hard surface coatings from these substrates without damage to the underlying material.

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Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

- 5 1. A composition for the selective removal of hard surface metal coatings, particularly ceramic, cermet and nickel-base mixtures, from high strength, high temperature resistant substrates, comprising:
 - about 90—450 g/l of H_2SO_4 ;
 - about 20—240 g/l of a water soluble nitro-substituted aromatic compound;
 - the remainder being water.
- 10 2. A composition as claimed in claim 1 wherein the solution further includes up to about 70 g/l of a water soluble fluorine-containing species which disassociates to provide a source of fluoride ions in solution.
- 15 3. A composition as claimed in claim 1 or claim 2 wherein the solution further includes up to about 3.0 g/l of a surfactant selected from the class of diphenylether sulfonates.
4. A composition for the selective removal of hard surface metal coatings, particularly ceramic, cermet and nickel-base mixtures, from high strength, high temperature resistant substrates, wherein the composition comprises:
 - about 250—300 g/l of H_2SO_4 ;
 - about 60—120 g/l of a water soluble nitro-substituted benzene compound;
 - about 10—20 g/l of a water soluble fluorine-containing species which disassociates to provide a source of fluoride ions in solution;
 - up to about 1.0 g/l of a surfactant selected from the class of diphenylether sulfonates;
 - the remainder being water.
- 25 5. A composition as claimed in claim 4 wherein the composition comprises about 270—280 g/l of H_2SO_4 .
6. A composition as claimed in claim 4 wherein the water soluble nitro-substituted benzene compound is about 100—120 g/l of meta-nitrobenzene sodium sulfonate.
- 30 7. A composition as claimed in claim 4 wherein the water soluble fluorine-containing species is about 10—20 g/l of fluoroboric acid.
8. A composition as claimed in claim 4 wherein the diphenylether sulfonate is up to about 0.5 g/l of sodium diphenylether sulfonate.
9. A composition as claimed in claim 1 or claim 4 substantially as hereinbefore described with particular reference to the Examples.
- 35 10. A composition as claimed in claim 1 or claim 4, substantially as illustrated in any one of the Examples.
11. A method for the selective removal of hard surface metal coatings, including ceramic, cermet and nickel-base mixtures from high strength, high temperature resistant substrates, the method comprising contacting the hard surface coating with an acidic stripping solution as claimed in any one of claims 1 to 10, in a suitable container means which is kept at a solution temperature of about 120—180°F and is continually agitated by an ultrasonic agitation means;
 - continuing the contacting until the hard surface coating has been substantially removed from the metal substrate without damaging the underlying substrate;
 - removing the substrate from the solution bath.
- 45 12. A method as claimed in claim 11 wherein the temperature of the solution is kept at about 130—150°F during operation.
13. A method as claimed in claim 11 or claim 12 wherein the ultrasonic agitation means is an ultrasonic generator-transducer which continually supplies a power density to the solution of at least 4 watts/in² during operation.
- 50 14. A method as claimed in claim 13 wherein the transducer is kept at a power density of about 7—8 watts/in².
15. A method as claimed in claim 11 substantially as hereinbefore described with particular reference to the Examples.
16. A method as claimed in claim 11 substantially as illustrated in any one of the Examples.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained